X-ray reflectivity investgation of structure and kinetics of photoswitchable lipid monolayers

Chatterjee, Kuntal; Haushahn, Björn; Shen, Chen; Festersen, Sven; Warias, Jonas; Runge, Benjamin; Reise, Franziska; Lindhorst, Thisbe; Klösgen, Beate; Magnussen, Olaf M.; Murphy, Bridget

DOI:
http://www.dpg-verhandlungen.de/year/2016/conference/regensburg/part/bp/session/19

Publication date:
2016

Document version
Final published version

X-Ray Reflectivity Investigation of Structure and Kinetics of Photoswitchable Lipid Monolayers

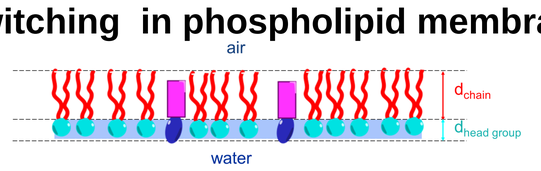
Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät
Institut für Experimentelle und Angewandte Physik

Kuntal Chatterjee[1] , Björn Haushahn[1], Chen Shen[1,3], Sven Festersen[1], Jonas Warias[1], Benjamin Runge[1], Franziska Reise[4], Thisbe Lindhorst[4], Beate. Klösgen[3], Olaf. M. Magnussen[1] and Bridget M. Murphy[1,2]

1: Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Germany.
2: Ruprecht Heansel Laboratory, University of Kiel, 24098 Kiel, Germany
3: Department of Physics, Chemistry and Pharmacy & MEMPHYS, University of Southern Denmark, Odense, Denmark.
4: Otto Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, Germany.

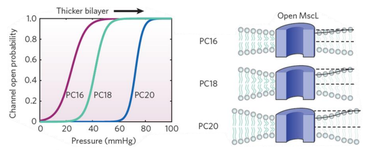
Introduction

Photoswitching in phospholipid membranes



Aim: understand role of lipids in cell signalling by investigating the molecular structure and membrane kinetics

Future applications for drug delivery



Emerging roles for lipids in shaping membrane-protein function

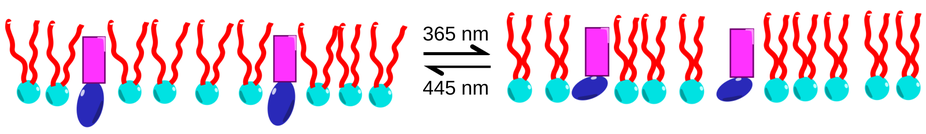
(a): lipid chain thickness

(b): lipid chain elasticity

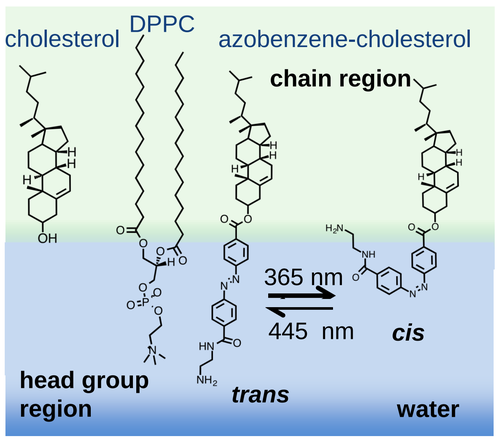
Phillips, Ursell, Wiggins, Sens, *Nature* **2009**, 459, 379-385

Photoswitchable Molecules

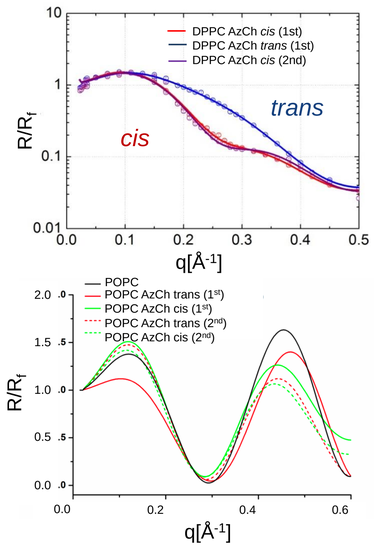
Photoswitching in phospholipid monolayers



Reversible conformation switching DPPC containing 5% azobenzene cholesterol (B09) monolayer on H_2O



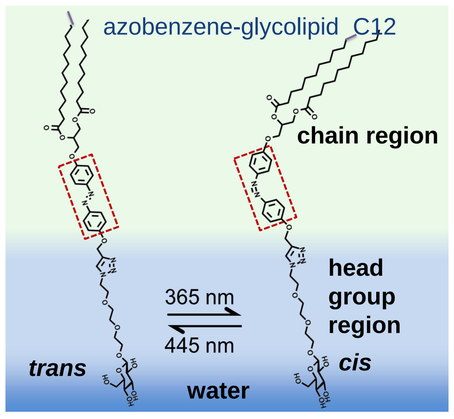
X-ray reflectivity



Switching in AzCh containing POPC

Jorgensen, Master's thesis, USD 2011

Azobenzene glycolipid (**azo-glyco)** glycoconjugate amphiphile photoswitchable azobenzene isomer in tail



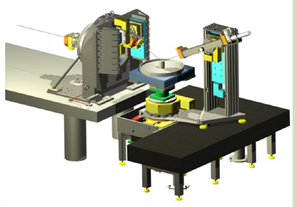
azo-glyco with a chain containing 12 and 16 carbon atoms

1,2-dipamitol-phosphatidylcholine (**DPPC**) monolayers at the air-water interface model membrane.

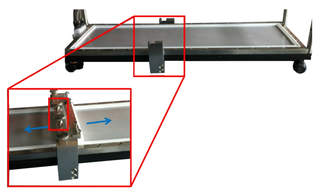
LISA at P08, PETRA III

Double crystal beam tilter in Bragg geometry:

- Studies of liquid-liquid and liquid-gas interfaces
- X-ray reflectivity without sample movement
- Grazing incidence diffraction
- High precision beam positioning
- Fast 2D detector (Eiger 1m)

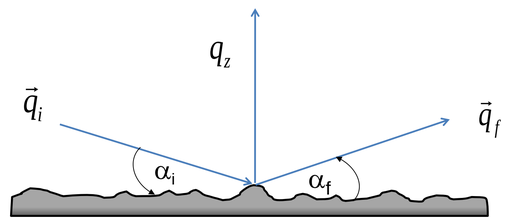


Langmuir Trough with Temperature control

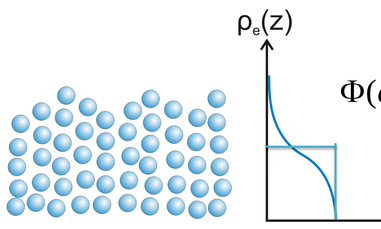


A novel X-ray diffractometer for studies of liquid-liquid interfaces, B.M. Murphy, M. Greve, B. Runge, C.T. Koops, A. Elsen, J. Stettner, O.H. Seeck, and O.M. Magnussen, *J. Synchrotron Rad.*, **21**, 45 (2014)

X-Ray Reflectivity at Liquid Interfaces



$R_f(q_z)$ = Fresnel reflectivity, $R(q_z)$ = measured reflectivity, q_z = momentum transfer, $\Phi(q_z)$ = liquid structure factor γ = surface tension, T = temperature, $CW(q, T, \gamma)$ = capillary wave component



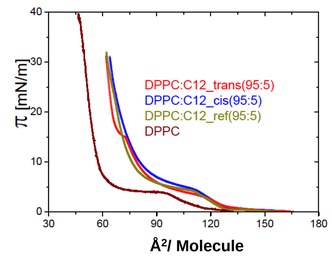
$$\Phi(q_z) = \frac{1}{\rho_\infty}\int dz \frac{d\langle\rho(z)\rangle}{dz}\exp(iq_z z)$$

$\rho_{e,\infty}$ = bulk density
$\rho_e(z)$ = local density

Experimental Results

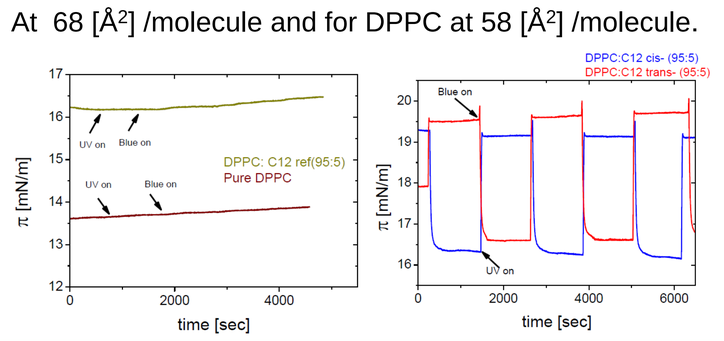
Langmuir Isotherm

- DPPC : nosurface pressure π [mN/m] increase
- trans- : has one extra phase transition
- cis- : higher π than trans-



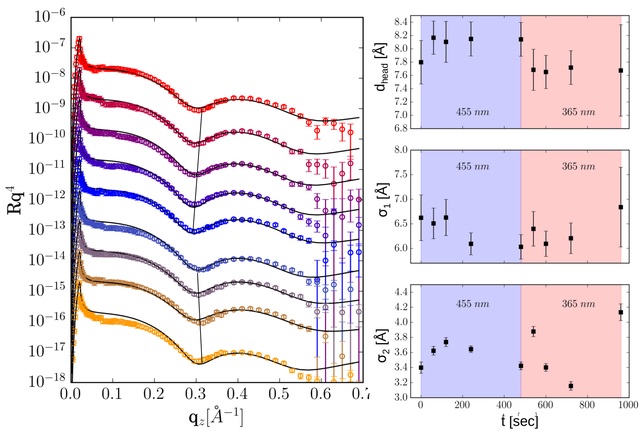
Switching Experiment

At 68 [Å²] /molecule and for DPPC at 58 [Å²] /molecule.

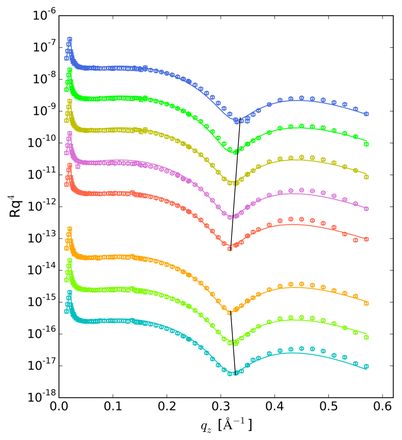


X-Ray Reflectivity

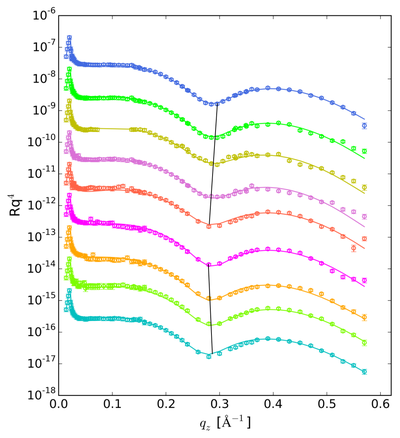
Azo-glyco C16 at 15mN/m



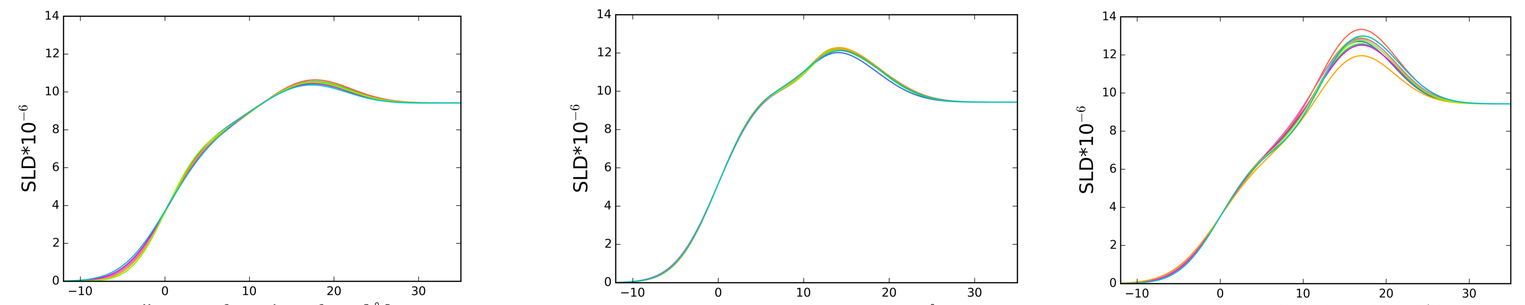
Azo-glyco C12 at 10mN/m



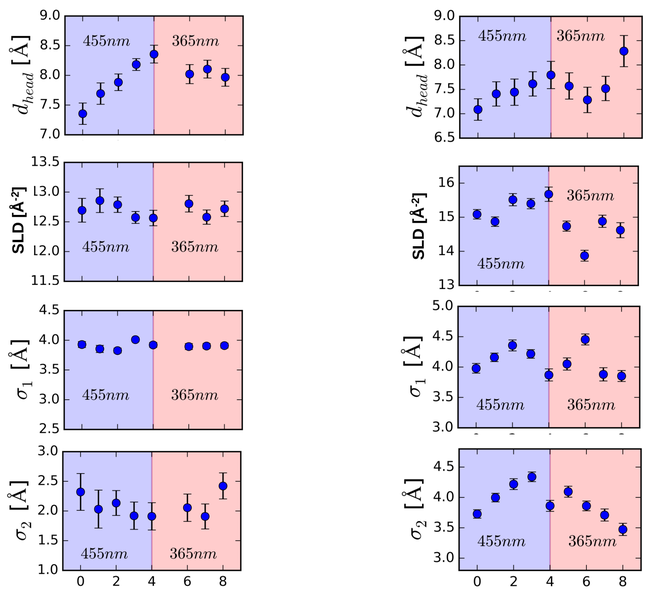
Azo-glyco C12 at 15mN/m



S0, t = 0s
S1, t = 60s
S2, t = 60s
S3, t = 120s
S4, t = 240s
S5, t = 60s
S6, t = 60s
S7, t = 120s
S8, t = 240s



Monolayer	Tail Length (Å)	Scattering Length Density Tail (SLD) (*10^-6) (Å^-2)	SLD Subphase (*10^-6) (Å^-2)	Roughness (σ) (Å)
π=10[mN/m]				
DPPC: C12 (95:5)	11.06	10.33	9.43	3.95
π=15[mN/m]				
DPPC: C12 (95:5)	12.45	7.02	9.43	3.95
DPPC: C16 (95:5)	12.27	7.04	9.42	4.12



illumination steps

Conclusion

- Changes in surface pressure during photoswitching
- Cis- isomer occupy more area ⟹ increase in π
- Both azo-glyco C12 and C16 are photoswitchable
- Structural changes can clearly be seen by X-ray reflectivity
- For both azo-glyco C12 and C16the head length increases when we photo switch from cis to trans and decreases when switched back

Acknowledgement

We thank Uta Rütt, David Reuther, Rene Kirchhof and the staff at P08
This work is funded by DFG SFB 677